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Shunpei YAMAZAKI et al.)
Serial No. 08/907,182) Art Unit: 1753
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For: THIN-FILM PHOTOELECTRIC)
CONVERSION DEVICE AND A METHOD)
OF MANUFACTURING THE SAME)

TC 1700 MAIL ROOM
JAN 27 2000

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VERIFICATION OF TRANSLATION

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

I, Kumiko Watanabe, 2-B, 1551, Hase, Atsugi-shi, Kanagawa-ken 243-0036 Japan, a translator, herewith declare:

that I am well acquainted with both the Japanese and English Languages;

that I am the translator of the attached translation of the Japanese Patent Application No. 7-110121 filed on April 11, 1995; and

that to the best of my knowledge and belief the following is a true and correct translation of the Japanese Patent Application No. 7-110121 filed on April 11, 1995.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: this 20th day of October, 1999

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[DOCUMENT NAME] Specification

[TITLE OF INVENTION] THIN FILM SOLAR CELL

[WHAT IS CLAIMED IS:]

[Claim 1]

5 A thin film solar cell comprising:

 a substrate;

 at least an amorphous silicon and a catalyst element formed adjacent to said amorphous silicon on said substrate; and

10 a crystalline silicon film formed by heat treatment of said amorphous silicon and said catalyst element,

 wherein said crystalline silicon contains a catalyst element at a concentration not higher than 5×10^{18} atoms/cm³.

[Claim 2]

15 A thin film solar cell comprising:

 a substrate;

 at least a first crystalline silicon film having a substantially intrinsic conductivity type and a second crystalline silicon film having one conductivity type on said substrate;

20 wherein said first crystalline silicon film contains a catalyst element for promoting crystallization of silicon at a concentration not higher than 5×10^{18} atoms/cm³.

[Claim 3]

25 A thin film solar cell comprising:

 a substrate;

 at least a first crystalline silicon film having a substantially intrinsic conductivity type and a second crystalline silicon film having one conductivity type on said substrate;

30 wherein said first crystalline silicon film contains a catalyst element for promoting crystallization of silicon at a concentration not higher than 5×10^{18} atoms/cm³,

wherein said second crystalline silicon film contains a catalyst element for promoting crystallization of silicon at a concentration higher than said first crystalline silicon film.

[Claim 4]

5 The thin film solar cell of claim 1 or claim 2 wherein said first crystalline silicon film has a different conductivity type than said second crystalline silicon film.

[Claim 5]

10 The thin film solar cell of claims 1 to 4 wherein said first crystalline silicon film having one conductivity type or a substantially intrinsic conductivity type comprises a plurality of crystal grains in the form of needles.

[Claim 6]

15 The thin film solar cell of claims 1 to 4 wherein said catalyst for promoting crystallization of silicon is a kind of element or several kinds of elements selected from the group consisting of Fe, Co, Ni, and Pt.

[DETAILED DESCRIPTION OF INVENTION]

[0001]

[FIELD FOR INDUSTRIAL USE]

20 The present invention relates to a thin film solar cell which is formed on a substrate, and more particularly to a thin film solar cell having a photoelectric conversion layer formed of a crystalline silicon film.

[0002]

25 [PRIOR ART]

A solar cell can be manufactured using a variety of semiconductor materials or organic compound materials. However, from the industrial viewpoint, silicon which is of a semiconductor is mainly used. The solar cells using silicon can be classified into a bulk solar cell using a wafer of 30 monocrystalline silicon or polycrystalline silicon and a thin film solar cell having a silicon film formed over a substrate. The reduction of manufacture costs is required, and the thin film solar cell is expected in

the effect of reducing the costs because raw materials are less used for the thin film solar cell than that for the bulk solar cell.

In the field of thin film solar cell, an amorphous silicon solar cell has been put into practical use. However, since the amorphous silicon 5 solar cell is lower in conversion efficiency compared with the monocrystalline silicon or polycrystalline silicon solar cell and also suffers from problems such as the deterioration due to light and so on, the use thereof is limited. For that reason, as another means, a thin-film solar cell using a crystalline silicon film has been also developed.

10 [0003]

A melt recrystallization method and a solid-phase growth method are used for obtaining a crystalline silicon film in the thin-film solar cell. Both the methods are that an amorphous silicon is formed over a substrate and recrystallized, thereby obtaining a crystalline silicon film. 15 In any event, the substrate is required to withstand the crystallization temperature, whereby usable material is limited. In particular, in the melt recrystallization method, the substrate has been limited to a material that withstands 1,412 °C, which is the melting point of silicon.

The solid-phase growth method is of a method in which an 20 amorphous silicon film is formed over the substrate and crystallized thereafter through a heat treatment. In such a solid-phase growth method, in general, as the temperature becomes high, the processing time may be shortened more. However, the amorphous silicon film has been hardly crystallized at a temperature of 500 °C or lower. For 25 example, when the amorphous silicon film which has been deposited through a vapor phase growth method is heated at 600 °C so as to be crystallized, 10 hours are required. Also, when the heat treatment is conducted at the temperature of 550 °C, a 100 hours or longer are required for the heat treatment.

30 [0004]

For the above reason, a high heat resistance has been required for the substrate of the thin-film solar cell. Therefore, glass, carbon or

ceramic was used for the substrate. However, from the viewpoint of reducing the costs of the solar cell, those substrates are not always proper, and it has been desired that the solar cell is manufactured on a substrate which is most generally used and inexpensive. However, for 5 example, the #7059 glass substrate made by Corning, which is generally used, has a distortion temperature of 593 °C, and the conventional crystallization technique allows the substrate to be distorted and largely deformed. For that reason, such a substrate could not be used. Also, since a substrate made of a material essentially different from silicon is 10 used, monocrystal cannot be obtained even through crystallization is conducted through the above means, and silicon having large crystal grains is hard to obtain. Consequently, this causes a limit to an improvement in the efficiency of the solar cell.

[0005]

15 In order to solve the above problems, a method of crystallizing an amorphous silicon film through a heat treatment is disclosed in Japanese patent laid-open publication No. Hei 7-58338. According to the method disclosed in this patent, in order to accelerate crystallization at a low temperature, a small amount of metal elements are added as a catalyst 20 material. Further, there is disclosed that the lowering of a heat treatment temperature and the reduction of a treatment time are enabled. For example, it is recognized that the crystallization can be done with four hours heat treatment when heat temperature is at 550 °C. Also, there is disclosed in the publication that a simple substance of 25 nickel (Ni), iron (Fe); cobalt (Co) or platinum (Pt), or a compound of any one of those materials with silicon, or the like is suitable for the catalyst material.

[0006]

[PROBLEMS PRESENT INVENTION INTENDS TO SOLVE]

30 However, since any catalyst material used for accelerating crystallization is a material which is naturally undesirable for crystalline silicon, it has been desired that the concentration is as low as possible.

The concentration of a catalyst material necessary for accelerating crystallization is $1 \times 10^{17}/\text{cm}^3$ to $1 \times 10^{20}/\text{cm}^3$. However, even when the concentration is relatively low, since the above catalyst material is a heavy metal element, the material contained in silicon forms a defect level, thereby lowering the characteristic of a manufactured element.

5 [0007]

The principle of operation of a solar cell manufactured by forming a p-n junction can be roughly described as follows. The solar cell absorbs light and generates the charges of electrons/holes due to an absorbed light energy. The electrons move toward an n-layer side, and the holes move toward a p-layer side due to the drifts caused by a junction electric field and diffusion. However, when the defect level is high in silicon, the charges are trapped by the defect level while they are moving in the silicon, thereby disappearing. Therefore, the photoelectric conversion characteristics are caused to lower. A period of time since the electrons/holes generate until they disappear is called "a life time". In the solar cell, it is desirable that the lifetime is long. Hence, it has been necessary to reduce the heavy metal elements that generate the defect level in silicon as much as possible.

20 [0008]

The subject of the present invention in a method of manufacturing a thin-film solar cell is to keep the character of crystallization due to the above catalyst material and remove the catalyst material which has become unnecessary after the crystallization has been completed. And it is a purpose to obtain a solar cell which is excellent in the photoelectric conversion characteristics using the above method.

25 [0009]

[MEANS TO SOLVE PROBLEMS]

A thin film solar cell disclosed in the present specification is manufactured through a crystalline silicon film obtained using an amorphous silicon formed over the substrate and metal elements which become catalyst materials accelerating the crystallization of the

amorphous silicon with a heat treatment. The thin film solar cell has a characteristic of removing the above metal elements remaining in the crystal silicon film and lowering the concentration.

[0010]

5 As the metal element promoting the crystallization of a silicon, it is possible to use one or more kind of elements selected from iron (Fe), cobalt (Co), nickel (Ni), and platinum (Pt). Particularly, nickel is very useful in an aspect of the effect and repeatability. When a silicon is crystallized through above catalyst elements, the crystal structure
10 becomes a needle-like crystal.

[0011]

In the semiconductor technology the effect of impurity metal element segregation with phosphorus in a silicon is known as the gettering technique. As a result of an experiment of the present
15 invention, segregation of the above metal elements into an outside region of a photoelectric conversion layer consisting of a crystalline silicon can be performed by forming a silicon film or a silicon oxide film to which phosphorus (P) is doped abut on a region consisting of the photoelectric conversion layer with a heat treatment. The temperature
20 of this heat treatment was permitted at a degree the above amorphous silicon film is crystallized. Therefore, the gettering technique can be done in a process of crystallization simultaneously or after the crystallization as well.

[0012]

25 In order to form a layer phosphorus is doped, the implantation can be conducted directly into the above amorphous silicon or a crystalline silicon through an ion implantation method or a plasma doping method, and so on. Samely, the above metal element is segregated.

30 [0013]

Outline of the invention disclosed in the specification is described as follows.

in accordance with one aspect of the invention disclosed in the specification,

a thin film solar cell comprising:

a substrate;

5 at least an amorphous silicon and a catalyst element formed abut on the amorphous silicon are provided,

a thin film solar cell using a crystalline silicon formed by applying a heat treatment to the above amorphous silicon and a catalyst element,

the above crystalline silicon includes the above catalyst element
10 and has a character that the concentration of the catalyst element is not higher than $5 \times 10^{18}/\text{cm}^3$.

[0014]

In accordance with another aspect of the invention disclosed in the specification,

15 a thin film solar cell comprising:

a substrate;

at least a first crystalline silicon film having a substantially intrinsic first crystalline silicon film and a second crystalline silicon film having one conductivity type;

20 the first crystalline silicon film contains a catalyst element promoting crystallization of a silicon at a concentration not higher than $5 \times 10^{18}/\text{cm}^3$.

[0015]

In accordance with still another aspect of the invention disclosed
25 in the specification, a thin film solar cell comprises at least a substantially-intrinsic first crystalline silicon film and a second crystalline silicon film having one conductivity type on the substrate. The first crystalline silicon film contains a catalyst element for promoting crystallization of a silicon at a concentration not higher than 5×10^{18} atoms/ cm^3 , and the second crystalline silicon film contains a catalyst element promoting crystallization of a silicon at a concentration higher than that of the first crystalline silicon film.

[0016]

The concentration value disclosed in the present specification is determined by a secondary ion mass spectroscopy and corresponds to a maximum value of the measured values.

5

[0017]

[OPERATION]

In accordance with a method of the present invention, concerning about a crystalline silicon film obtained by doping a catalyst material to an amorphous silicon with a heat treatment, the catalyst material remained inside of the crystalline silicon film could be removed by providing a semiconductor layer or an insulating layer containing phosphorus abut on the crystalline silicon film and segregating the catalyst material into the above layer. As a result of that, a carrier life time of the above crystalline silicon film becomes longer and good character of a thin film solar cell is obtained.

10
15 [0018]

[EMBODIMENT]

[First Embodiment]

The example shows a process of manufacturing a thin-film solar cell which is manufactured through a method of forming an amorphous silicon film in close contact with metal elements that accelerate the crystallization of silicon, crystallizing said amorphous silicon film through a heat treatment, and removing said metal elements remaining in the crystallized silicon film after the crystallization.

20
25

[0019]

This embodiment will be described with reference to Fig.1. In this embodiment, nickel is used as metal elements having a catalytic action that accelerates the crystallization of silicon. First, a silicon oxide film 102 having a thickness of 0.3 µm is formed over a glass substrate (for example, Corning 7059 glass substrate) 101 as an base film. The silicon oxide film 102 is formed through a plasma CVD technique with a raw

material of tetra ethoxy silane (TEOS), and also can be formed through a sputtering technique as another method. Subsequently, an amorphous silicon film 103 is formed with a raw material of silane gas through a plasma CVD method. The formation of the amorphous silicon film may 5 be conducted using a low pressure thermal CVD method, a sputtering method or an vacuum evaporation method. The above amorphous silicon film may be a substantially-intrinsic amorphous silicon film or may contain boron (B) at 0.001 to 0.1 atms%. Also, the thickness of the amorphous silicon film 103 is set to 10 μm . It is needless to say that the 10 thickness may be set to a required one (Fig. 1(A)).

[0020]

Subsequently, the substrate is immersed in an ammonium hydroxide and held at 70 °C for 5 minutes, to thereby form an oxide film (not shown in a figure) on the surface of the amorphous silicon film 103. 15 This oxide film is formed in order to improve its wettability in a process of coating nickel acetate solution which will be conducted later. Furthermore, the nickel acetate solution is coated on the surface of the amorphous silicon film by spin coating. The nickel element functions as an element that accelerates the crystallization in crystallizing the 20 amorphous silicon film.

[0021]

Subsequently, the amorphous silicon film is held at a temperature of 450 °C for one hour in a nitrogen atmosphere, thereby eliminating hydrogen from the amorphous silicon film. This is because dangling 25 bonds are intentionally produced in the amorphous silicon film, to thereby lower a threshold energy in crystallization later. Then, the amorphous silicon film 103 is subjected to a heat treatment at 550 °C for 4 to 8 hours in the nitrogen atmosphere, to thereby crystallize the amorphous silicon film 103. A temperature in crystallizing can be set to 30 550 °C because of the action of nickel elements. Hydrogen of 0.001 atms% to 5 atms% is contained in a crystalline silicon film which has

been crystallized. During the above heat treatment, nickel element accelerates the crystallization of the crystalline silicon film while it is moving in the silicon film.

[0022]

5 In this way, the crystalline silicon film is formed on the glass substrate. Subsequently, a phosphorus silicate glass (PSG) 104 is formed on the crystalline silicon film 103. The phosphorus silicate glass (PSG) 104 is formed, using a mixture gas consisting of silane, phosphine and oxygen, at a temperature of 450 °C through an atmospheric pressure
10 CVD method. The concentration of phosphorus in the phosphorus silicate glass is set to 1 to 30 wt%, preferably 7 wt%. The phosphorus silicate glass 104 is to getter nickel remaining in the crystalline silicon film. Even though the phosphorus silicate glass is merely formed at 450 °C, its effect is obtained. More effectively, it is good to conduct a heat
15 treatment at a heat treatment temperature of 500 to 800 °C, preferably 550 °C for 1 to 4 hours in the nitrogen atmosphere. As another method, the phosphorus silicate glass can be replaced by a silicon film to which phosphorus of 0.1 to 10 wt% has been added with the same effect (Fig. 1(B)).

20 [0023]

Thereafter, the phosphorus silicate glass 104 is etched using a hydrogen fluoride aqueous solution so as to be removed. As a result, the surface of the crystalline silicon film 103 is exposed over the main surface of the substrate 101. On that surface is formed an n-type
25 crystalline silicon film 105. The n-type crystalline silicon film 105 may be formed through a plasma CVD method or through a low pressure thermal CVD method. The n-type crystalline silicon film is desirably formed at a thickness of 0.02 to 0.2 μm, and in this embodiment, it is formed at a thickness of 0.1 μm (Fig. 1(C)).

30 [0024]

Then, a transparent electrode 106 is formed on the n-type crystalline silicon film 105. The transparent electrode 106 is made of indium tin oxide alloy (ITO) and has a thickness of 0.08 µm through a sputtering method. Finally, a process of providing lead electrodes is 5 conducted. In providing the lead electrodes, as shown in Fig. 1(D), a minus side electrode is provided on the transparent electrode 106, and a plus side electrode is provided by removing the parts of the transparent electrode 106, the n-type crystalline silicon 105 and crystalline silicon 103. The lead electrodes 107 can be formed by sputtering method or 10 vacuum evaporation method using aluminum, silver, silver paste or the like. Furthermore, after the provision of the electrodes, the product is subjected to a heat treatment at 150 °C to 300 °C for several minutes with the result that the adhesion to the base film becomes high, thereby 15 obtaining an excellent electric characteristic. In this embodiment, the product is subjected to a heat treatment at 200 °C for 30 minutes in a nitrogen atmosphere using an oven.

Through the above-mentioned processes, a thin-film solar cell is completed.

[0025]

20 (Second Embodiment)

In a second embodiment, there is shown a thin-film solar cell which was formed in the process where a metal element that accelerates the crystallization of silicon is removed after crystallization through the method where phosphorus is implanted through a plasma doping 25 method into the surface of crystalline silicon film.

[0026]

A second embodiment will be described with reference to Figs. 2. Nickel is used to accelerate the crystallization of silicon as a metal element working as a catalyst in this embodiment. First, a silicon oxide 30 film 202 having a thickness of 0.3 µm is formed on a glass substrate (for example, Corning 7059 glass substrate) 201 as a base film.

The silicon oxide film is formed by plasma CVD method with a raw material of tetra ethoxy silane (TEOS), and also can be formed through a sputtering method as another method. Subsequently, an amorphous silicon film 203 is formed with a raw material of silane gas through a 5 plasma CVD method. The formation of the amorphous silicon film may be conducted using a low pressure thermal CVD method, a sputtering method or an vacuum evaporation method. The above amorphous silicon film may be a substantially-intrinsic amorphous silicon film or an amorphous silicon film to which boron (B) of 0.001 to 0.1 atms% has 10 been added. Also, the thickness of the amorphous silicon film 203 is set to 20 μm . It is needless to say that the thickness may be set to a required one (Fig. 2(A)).

[0027]

Thereafter, the substrate is immersed in an ammonium hydroxide 15 at 70 $^{\circ}\text{C}$ for 5 minutes, to thereby form an oxide film (not shown in the figure) on the surface of the amorphous silicon film 103. The silicon oxide film is formed in order to improve its wettability in a process of coating nickel acetate solution which will be conducted later. Furthermore, the nickel acetate solution is coated on the surface of the 20 amorphous silicon film by spin coating method. The nickel element functions as an element that accelerates the crystallization in crystallizing the amorphous silicon film.

[0028]

Subsequently, the amorphous silicon film is held at a temperature 25 of 450 $^{\circ}\text{C}$ for one hour in a nitrogen atmosphere, thereby eliminating hydrogen from the amorphous silicon film. This is because dangling bonds are intentionally produced in the amorphous silicon film, to thereby lower a threshold energy in later crystallization. Then, the amorphous silicon film 203 is subjected to a heat treatment at 550 $^{\circ}\text{C}$ for 30 4 to 8 hours in a nitrogen atmosphere, to thereby crystallize the amorphous silicon film 203. A temperature in the crystallization can be

set to 550 °C because of the action of nickel elements. Hydrogen of 0.001 atms% to 5 atms% is contained in a crystalline silicon film 203 which has been crystallized. During the above heat treatment, nickel element accelerates the crystallization of the crystalline silicon film
5 while it is moving in the silicon film.

[0029]

In this way, the crystalline silicon film can be formed on the glass substrate. In this state, the implantation of phosphorus (P) ions is conducted by a plasma doping method. The dose amount may be set to 10 1×10^{14} to $1 \times 10^{17} /cm^2$, and in this embodiment, it is set to $1 \times 10^{16} /cm^2$. An accelerating voltage is set to 20 keV. Through this process, a layer containing phosphorus with a high concentration therein is formed within a region of 0.1 to 0.2 μm to the depth direction from the surface of the crystalline silicon film 203. Thereafter, a heat treatment is
15 conducted in order to getter nickel remaining in the crystalline silicon film. The crystalline silicon film may be subjected to a heat treatment at 500 to 800 °C, preferably 550 °C for 1 to 4 hours in the nitrogen atmosphere (Fig. 2(B)).

[0030]

Since a region into which phosphorus ions have been implanted has crystal destroyed, it becomes of a substantially amorphous structure immediately after the ions have been implanted thereinto. Thereafter, since that region is crystallized through said heat treatment, it is usable as the n-type layer of the solar cell even in this state. In the phosphorus doped region, since nickel as a catalyst element segregates and they are desirably to be removed. As the removing method, after a natural oxide film thinly formed on the surface has been etched using a hydrogen fluoride aqueous solution, it is removed using sulfur hexafluoride and nitric trifluoride through by dry etching method. With this process, the
25 surface of the crystalline silicon film 203 is exposed over the main surface of the substrate 201. On that surface is formed an n-type
30

crystalline silicon film 204. The n-type crystalline silicon film 204 may be formed by plasma CVD method or low pressure thermal CVD method. The n-type crystalline silicon film is desirably formed at a thickness of 0.02 to 0.2 μm , and in this embodiment, it is formed at a thickness of 0.1 5 μm (Fig. 2(C)).

[0031]

Then, a transparent electrode 205 is formed on the above n-type crystalline silicon film 204. The transparent electrode 205 is made of indium tin oxide alloy (ITO) and has a thickness of 0.08 μm through a 10 sputtering method. Finally, a process of providing lead electrodes is conducted. In providing the lead electrodes, as shown in Fig. 2(D), a minus side electrode is provided on the transparent electrode 107, and a plus side electrode is provided by removing the parts of the transparent electrode 205, the n-type crystalline silicon 204 and crystalline silicon 15 203. The lead electrodes 206 can be formed through a sputtering method or a vacuum evaporation method using aluminum, silver, silver paste or the like. Furthermore, after the provision of the electrodes, a heat treatment at 150 °C to 300 °C for several minutes is conducted with the result that the adhesion to the base film becomes high, thereby 20 obtaining an excellent electric characteristic. In this embodiment, a heat treatment is conducted at 200 °C for 30 minutes in a nitrogen atmosphere using an oven.

Through the above-mentioned processes, a thin-film solar cell is completed.

25 [0032]

(Third Embodiment)

A third embodiment shows an example where in the process of manufacturing the thin-film solar cell described with reference to the first and second embodiments, the surface of the crystalline silicon film 30 is subjected to an anisotropic etching process so as to make the surface of the solar cell irregular as shown in Fig. 3. A technique by which that

surface is made irregular so that the reflection from the surface of the solar cell is reduced is called "a texture treatment".

[0033]

A silicon oxide film 302 having a thickness of 0.3 μm is formed on 5 a glass substrate (for example, Corning 7959 glass substrate) 301 as a base film 302. The silicon oxide film is deposited by plasma CVD method with a raw material of tetra ethoxy silane (TEOS), and also can be formed by sputtering method as another method. Subsequently, an amorphous silicon film 303 is deposited by plasma CVD method. The 10 formation of the amorphous silicon film 303 may be conducted by low pressure thermal CVD method, sputtering method, vacuum evaporation method or the like. The above amorphous silicon film may be a substantially-intrinsic amorphous silicon film or an amorphous silicon film to which boron (B) of 0.001 to 0.1 atms% has been added. Also, the 15 thickness of the amorphous silicon film is set to 20 μm . It is needless to say that the thickness may be set to a required one.

[0034]

Subsequently, the substrate is immersed in an ammonium hydroxide and then held at 70 °C for 5 minutes, to thereby form an 20 oxide film on the surface of the amorphous silicon film 303. The oxide film is formed in order to improve its wettability in a process of coating nickel acetate solution which will be conducted later. Furthermore, the nickel acetate solution is coated on the surface of the amorphous silicon film by spin coating. The nickel element functions as an element that 25 accelerates the crystallization in crystallizing the amorphous silicon film.

[0035]

Subsequently, the amorphous silicon film is held at a temperature 30 of 450 °C for one hour in a nitrogen atmosphere, thereby eliminating hydrogen from the amorphous silicon film. This is because dangling bonds are intentionally formed in the amorphous silicon film, to thereby lower a threshold energy in later crystallization. Then, the amorphous

silicon film is subjected to a heat treatment at 550 °C for 4 to 8 hours in the nitrogen atmosphere, to thereby crystallize the amorphous silicon film. A temperature in crystallizing can be set to 550 °C because of the action of nickel elements. Hydrogen of 0.001 atms% to 5 atms% is contained in the crystalline silicon film which has been crystallized. During the above heat treatment, nickel elements accelerates the crystallization of the above crystalline silicon film while it is moving in the silicon film.

[0036]

In this way, the crystalline silicon film can be formed on the glass substrate. Then, a gettering process is conducted in order to remove nickel remaining in the crystalline silicon film. A method of conducting the gettering process may be a method of forming a phosphorus silicate glass (PSG) on the crystalline silicon film, or a method of conducting ion implantation of phosphorus into the surface of the crystalline silicon film.

[0037]

In a method of forming the phosphorus silicate glass (PSG), the phosphorus silicate glass film is formed, using a mixture gas consisting of silane, phosphine and oxygen, at a temperature of 450 °C through atmospheric pressure CVD method. The gettering treatment is conducted by a heat treatment at 550 °C for 1 to 4 hours in a nitrogen atmosphere. Thereafter, the phosphorus silicate glass is desirably etched using a hydrogen fluoride aqueous solution so as to be removed.

In the method of implanting phosphorus into the surface of the crystalline silicon film by ion implantation, the implantation of phosphorus can be conducted through plasma doping method. The dose amount may be set to 1×10^{14} to $1 \times 10^{17} /cm^2$, and in this embodiment, it is set to $1 \times 10^{16} /cm^2$. An accelerating voltage is set to 20 keV. Through this treatment, a layer containing phosphorus with a high concentration therein is formed within a region of 0.1 to 0.2 μm to

the depth direction from the surface of the crystalline silicon film. Thereafter, a heat treatment is conducted in order to getter nickel remaining in the crystalline silicon film. The heat treatment is conducted at a heat treatment temperature of 500 to 800 °C, preferably
5 550 °C for 1 to 4 hours in the nitrogen atmosphere.

[0038]

After the gettering treatment has been completed, the texture treatment is conducted on the surface of the crystalline silicon film. The texture treatment can be conducted using hydrazine or sodium
10 hydroxide aqueous solution. Hereinafter, a case of using sodium hydroxide will be described.

The texture treatment is conducted by heating an aqueous solution containing sodium hydroxide 2% in concentration to 80 °C. Under this condition, the etching rate of the crystalline silicon film thus obtained in this embodiment is about 1 μm/min. The etching is conducted for five minutes, and thereafter the crystalline silicon film is immersed in boiling water in order to immediately cease the reaction and sufficiently cleaned by flowing water. As a result of observing the surface of the crystalline silicon film which has been subjected to the
15 20 texture treatment through an electron microscope, the unevenness of about 0.1 to 5 μm is found on the surface although it is at random.

[0039]

On that surface is formed an n-type crystalline silicon film 304. The n-type crystalline silicon film may be formed through a plasma CVD method or through a low pressure thermal CVD method. The n-type crystalline silicon film 304 is desirably formed at a thickness of 0.02 to
25 0.2 μm, and in this embodiment, it is formed at a thickness of 0.1 μm.

[0040]

Then, a transparent electrode 305 is formed on the above n-type crystalline silicon film. The transparent electrode 305 is made of indium tin oxide alloy (ITO) and has a thickness of 0.08 μm by

sputtering method. Finally, a process of providing lead electrodes is conducted. In providing the lead electrodes, as shown by the structure in Fig. 3, a minus side electrode is provided on the transparent electrode, and a plus side electrode is provided by removing parts of the
5 transparent electrode, the n-type crystalline silicon and the crystalline silicon. The lead electrodes 306 can be formed by sputtering method or vacuum evaporation method using aluminum, silver, silver paste or the like. Furthermore, after the provision of the electrodes, a heat treatment at 150 °C to 300 °C is conducted for several minutes with the
10 result that the adhesion to the base film becomes high, thereby obtaining an excellent electric characteristic. In this embodiment, the heat treatment was conducted at 200 °C for 30 minutes in a nitrogen atmosphere using an oven.

Through the above-mentioned processes, a thin-film solar cell
15 having the texture structure on the surface is obtained.

[0041]

(Fourth Embodiment)

A fourth embodiment shows a technique of manufacturing a thin-film solar cell, as shown in Fig. 4, in which a coating of metal elements
20 that accelerate the crystallization of silicon is formed on a substrate, an amorphous silicon film is formed on the coating of the above metal elements, and the amorphous silicon film is crystallized through a heat treatment, and after crystallization, the metal elements diffused in the crystalline silicon film are removed therefrom.

[0042]

First, a coating of the metal element that accelerates the crystallization of silicon is formed over a substrate. Nickel is used as the metal element. A silicon oxide film having a thickness of 0.3 μm is first formed on a glass substrate (for example, Corning 7059 glass substrate)
30 401 as a base film 402. The silicon oxide film is formed through a plasma CVD method with a raw material of tetra ethoxy silane (TEOS),

and also can be formed through a sputtering method as another method. Subsequently, a nickel film 407 is formed over the substrate. The nickel film having 0.1 μm is formed using a tablet made of pure nickel through an electron beam vacuum evaporation method. Then, an amorphous 5 silicon film 403 is formed through a plasma CVD method. The formation of the amorphous silicon film may be conducted through low pressure thermal CVD method, sputtering method, vacuum evaporation method or the like. The above amorphous silicon film may be a substantially-intrinsic amorphous silicon film or an amorphous silicon film to which boron (B) of 0.001 to 0.1 atms% has been added. Also, the thickness of 10 the amorphous silicon film is set to 10 μm . It is needless to say that the thickness may be set to a required one.

[0043]

Subsequently, the amorphous silicon film is held at a temperature 15 of 450 °C for one hour in a nitrogen atmosphere, thereby eliminating hydrogen from the amorphous silicon film. This is because dangling bonds are intentionally formed in the amorphous silicon film, to thereby lower a threshold energy in later crystallization. Then, the amorphous silicon film is subjected to a heat treatment at 550 °C for 4 to 8 hours in 20 the nitrogen atmosphere, to thereby crystallize the amorphous silicon film. A temperature in crystallizing can be set to 550 °C because of the action of nickel elements. Hydrogen of 0.001 atms% to 5 atms% is contained in a crystalline silicon film which has been crystallized. During the above heat treatment, a small amount of nickel elements 25 diffuse from the nickel film disposed under the amorphous silicon film into the silicon film, and accelerates the crystallization of the crystalline silicon film while it is moving in the silicon film.

[0044]

In this way, the crystalline silicon film is formed over the glass 30 substrate. Subsequently, a phosphorus silicate glass (PSG) is formed on the crystalline silicon film. The phosphorus silicate glass (PSG) is

formed, using a mixture gas consisting of silane, phosphine and oxygen, at a temperature of 450 °C by atmospheric pressure CVD method. The concentration of phosphorus in the phosphorus silicate glass is set to 1 to 30 wt%, preferably 7 wt%. The phosphorus silicate glass is to getter 5 nickel remaining in the crystalline silicon film. Even though the phosphorus silicate glass is merely formed at 450 °C, its effect is obtained. More effectively, the phosphorus silicate glass may be subjected to a heat treatment at a heat treatment temperature of 500 to 800 °C, preferably 550 °C for 1 to 4 hours in the nitrogen atmosphere. 10 As another method, the phosphorus silicate glass can be replaced by a silicon film to which phosphorus of 0.1 to 10 wt% has been added with the same effect.

[0045]

Thereafter, the phosphorus silicate glass is etched using a 15 hydrogen fluoride aqueous solution so as to be removed. As a result, the surface of the crystalline silicon film is exposed over the main surface of the substrate. On that surface is formed an n-type crystalline silicon film 404. The n-type crystalline silicon film 404 may be formed by plasma CVD method or low pressure thermal CVD method. The n-20 type crystalline silicon film is desirably formed at a thickness of 0.02 to 0.2 μm, and in this embodiment, it is formed at a thickness of 0.1 μm.

[0046]

Then, a transparent electrode 405 is formed on the above n-type 25 crystalline silicon film. The transparent electrode 405 is made of indium tin oxide alloy (ITO) and has a thickness of 0.08 μm by sputtering method. Finally, a process of providing lead electrodes 406 is conducted. In providing the lead electrodes, as shown in Fig. 4, a minus side electrode is provided on the transparent electrode, and a plus side electrode is provided by removing parts of the transparent electrode, 30 the n-type crystalline silicon and the crystalline silicon. The lead electrodes can be formed by sputtering method or vacuum evaporation

method using aluminum, silver, silver paste or the like. Furthermore, after the provision of the lead electrodes, the substrate is subjected to a heat treatment at 150 °C to 300 °C with the result that the adhesion to the base film becomes high, thereby obtaining an excellent electric characteristic. In this embodiment, a heat treatment was conducted at 200 °C for 30 minutes in a nitrogen atmosphere using an oven.

Through the above-mentioned processes, a thin-film solar cell is completed.

[0047]

10 [EFFECT OF INVENTION]

As was described above, in the method of manufacturing the thin-film solar cell in accordance with the present invention, in a process of crystallizing an amorphous silicon film by a heat treatment, a catalyst material such as nickel is used, thereby making it possible to obtain a crystalline silicon film at a heat treatment temperature lower than the conventional method. Furthermore, the method of the present invention enables the concentration of the catalyst material remaining in the crystalline silicon film obtained to be lowered. As a result, a thin-film solar cell that uses an inexpensive glass substrate and is excellent in photoelectric conversion characteristic can be obtained.

20 [BRIEF DESCRIPTION OF DRAWINGS]

The above and other objects and features of the present invention will be more apparent from the following description taken in conjunction with the accompanying drawings.

25 Fig. 1 is a schematic diagram showing a method of manufacturing a thin-film solar cell in accordance with the present invention;

Fig. 2 is a schematic diagram showing a method of manufacturing a thin-film solar cell in accordance with the present invention;

30 Fig. 3 is a diagram showing one example of a cross-sectional structure of a thin-film solar cell in accordance with the present invention; and

Fig. 4 is a diagram showing one example of a cross-sectional structure of a thin-film solar cell in accordance with the present invention.

[DESCRIPTION OF MARKS]

- 5 101 ... substrate
- 102 ... silicon oxide layer
- 103 ... amorphous silicon layer or a crystalline silicon layer
- 104 ... phosphorus silicate glass (PSG)
- 105 ... n-type silicon layer
- 10 106 ... transparent electrode
- 107 ... lead electrode
- 201, 301, 401 ... substrate
- 202, 302, 402 ... silicon oxide layer
- 203, 303, 403 ... amorphous silicon layer or crystalline silicon layer
- 15 204, 304, 404 ... n-type silicon layer
- 205, 305, 405 ... transparent electrode
- 206, 306, 406 ... lead electrode
- 407 ... nickel film

[NAME OF THE DOCUMENT]

Abstract

[ABSTRACT]

[PURPOSE]

Reducing the concentration of the catalyst element in the film and
5 obtaining the desirable characteristics after the crystallization as of the
thin film solar cell which a catalyst element is added and manufactured
through a solid-phase growth method.

[STRUCTURE]

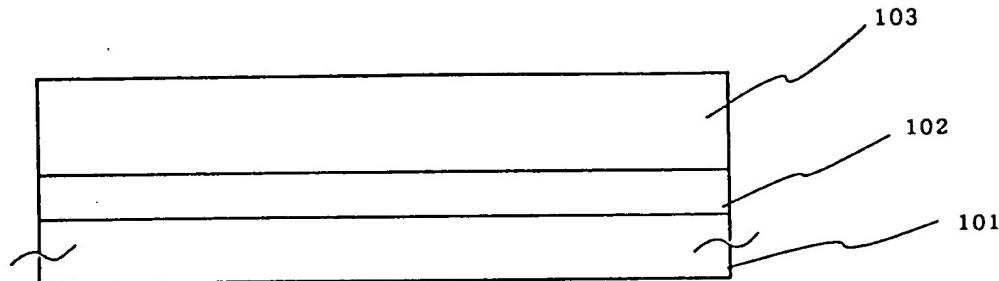
Forming the silicon oxide film 102 and the amorphous silicon film
10 103 on the substrate 101. Then, the amorphous silicon film is
crystallized by applying a catalyst element which accelerates the
crystallization with a heat treatment. Providing PSG layer or the like
abut on the obtained crystalline silicon film, the above catalyst element
15 is made to segregate by phosphorus gettering. As a result, the
concentration of the above catalyst element remaining in the crystalline
silicon film can be reduced. The thin film solar cell obtained shows a
desirable photo electric conversion character.

[SELECTED FIGURE]

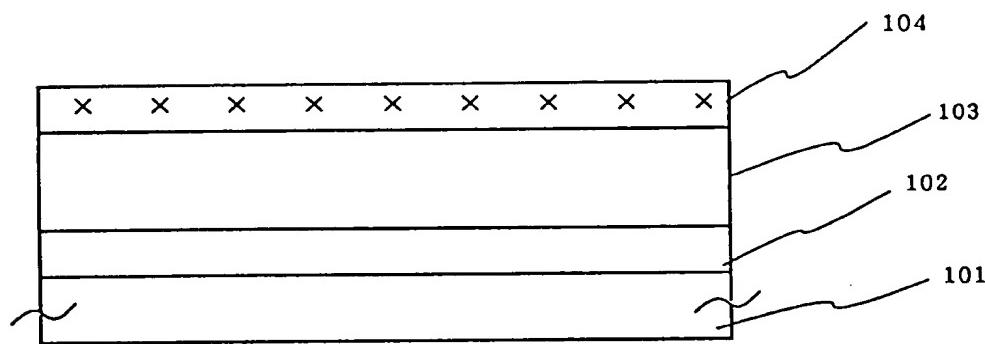
Fig. 1

【書類名】図面
【図1】

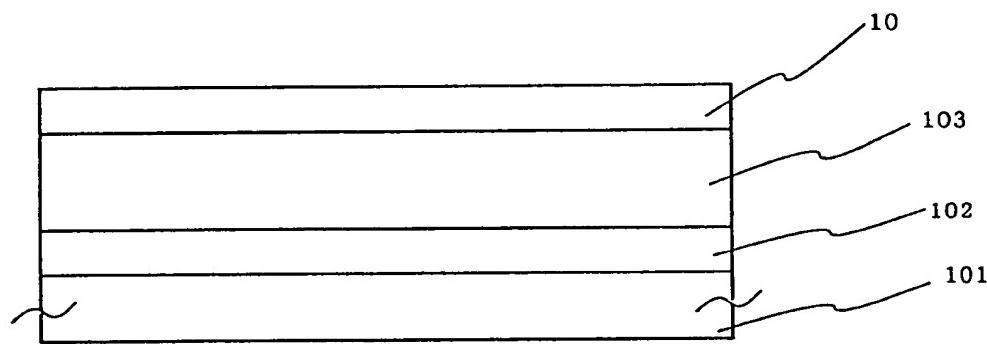
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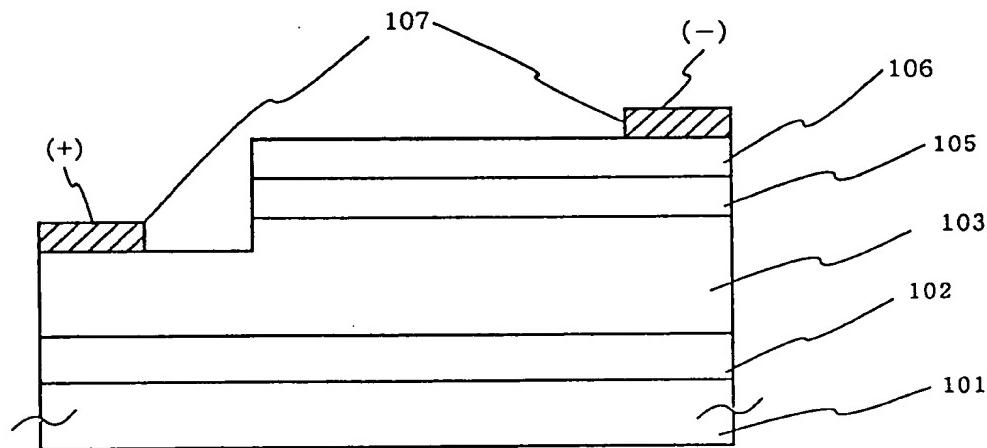
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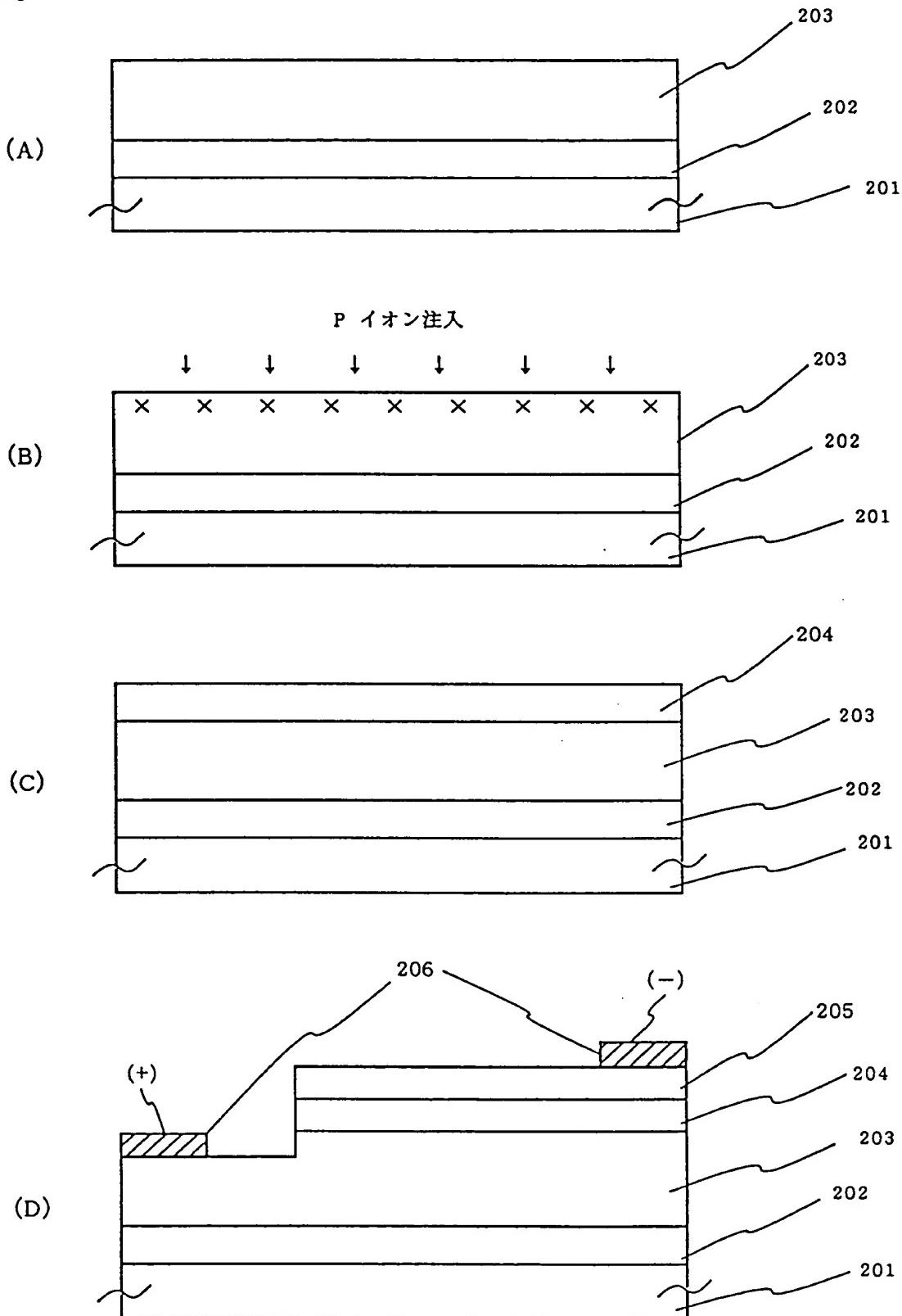


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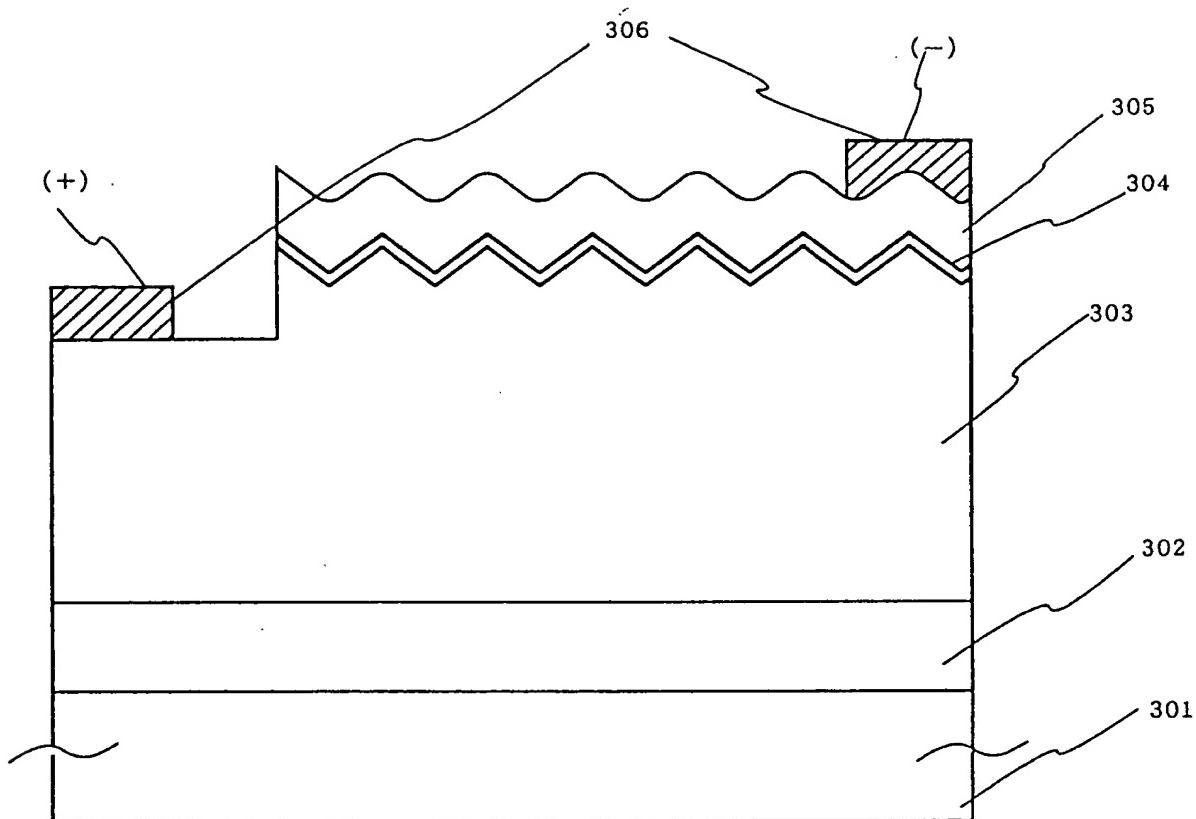
【整理番号】P002979-01

【図2】



【整理番号】P002979 - 01

【図3】



(整理番号) P002979 - 01

【図4】

